

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
15 May 2003 (15.05.2003)

PCT

(10) International Publication Number
WO 03/040251 A1

(51) International Patent Classification⁷: C09J 163/00,
C08K 5/18, C09J 7/04

MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD,
SE, SG, SL, SK (utility model), SK, SL, TJ, TM, TN, TR,
TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW.

(21) International Application Number: PCT/US02/30155

(84) Designated States (regional): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),
Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE,
ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK,
TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ,
GW, ML, MR, NE, SN, TD, TG).

(22) International Filing Date:
23 September 2002 (23.09.2002)

(25) Filing Language: English

Declarations under Rule 4.17:

(30) Priority Data:
10/005,556 8 November 2001 (08.11.2001) US

— as to applicant's entitlement to apply for and be granted
a patent (Rule 4.17(ii)) for the following designations AE,
AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH,
CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI,
GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG,
KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK,
MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD,
SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ,
VC, VN, YU, ZA, ZM, ZW, ARIPO patent (GH, GM, KE, LS,
MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent
(AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent
(AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB,
GR, IE, IT, LU, MC, NL, PT, SE, SK, TR), OAPI patent (BF,
BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN,
TD, TG)

(71) Applicant: 3M INNOVATIVE PROPERTIES COMPANY [US/US]; 3M Center, Post Office Box 33427, Saint Paul, MN 55133-3427 (US).

— as to the applicant's entitlement to claim the priority of the
earlier application (Rule 4.17(iii)) for all designations

(72) Inventors: GEORGE, Clayton, A.; Post Office Box 33427, Saint Paul, MN 55133-3427 (US). SCHULTZ, William, J.; Post Office Box 33427, Saint Paul, MN 55133-3427 (US). THOMPSON, Wendy, L.; Post Office Box 33427, Saint Paul, MN 55133-3427 (US).

(74) Agents: BARDELL, Scott, A. et al.; Office of Intellectual Property Counsel, Post Office Box 33427, Saint Paul, MN 55133-3427 (US).

(81) Designated States (national): AE, AG, AL, AM, AT (utility model), AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ (utility model), CZ, DE (utility model), DE, DK (utility model), DK, DM, DZ, EC, EE (utility model), EE, ES, FI (utility model), FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN,

Published:
— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: HIGH TEMPERATURE EPOXY ADHESIVE FILMS

(57) Abstract: The invention provides polyepoxide-based adhesives containing cycloaliphatic-containing polyepoxide resin, aromatic polyepoxide resin, and 9,9-bis(3-methyl-4-aminophenyl)fluorene. The adhesives provide improved peel and shear strength.

WO 03/040251 A1

HIGH TEMPERATURE EPOXY ADHESIVE FILMS

Field of the Invention

This invention relates to high temperature resistant epoxy-based adhesive films.

5

Background of the Invention

Polyepoxide resins are monomers or prepolymers that react with curing agents to yield high performance resins. These resins have gained wide acceptance in structural adhesives because of their combination of characteristics such as thermal and chemical 10 resistance, adhesion, and abrasion resistance.

Cured epoxy resins are frequently required to have high glass transition temperatures in order to provide adhesives having structural properties at high temperatures. Examples of methods of achieving high glass transition temperatures in such polyepoxide resins include: preparing resins having a high crosslink density and a 15 high concentration of polar groups as disclosed in U.S. Pat. No. 4,331,582; using epoxy resins compositions in which the epoxy-group containing compound contains a polycyclic structure, such as in U.S. Pat. Nos. 2,902,471; 3,298,998; and 3,332,908; using epoxy resin compositions in which the curing agent or hardener contains a polycyclic structure; and combining a 9,9-bis(aminophenyl)fluorene with an aromatic epoxy resin as described 20 in U.S. Pat. No. 4,684,678.

Although many of these compositions can be cured to resins having a high glass transition temperature, the cured resins typically are highly crosslinked, and are brittle or have a low ductility. One method of improving the ductility of such cured resins is by adding a rubber component or toughening agent to the composition. However, many 25 compositions containing cured epoxy resins having a high glass transition temperature are incompatible with such toughening agents.

Summary of the Invention

In one aspect, the invention provides an adhesive composition comprising a 30 mixture of polyepoxide resins comprising cycloaliphatic-containing polyepoxide resin and aromatic polyepoxide resin and an effective amount of 9,9-bis(3-methyl-4-aminophenyl)fluorene. The mixture of polyepoxide resins has a cycloaliphatic character

of greater than 10 weight percent, as defined below. The cycloaliphatic-containing polyepoxide resin is present in the adhesive composition in an amount of at least 20 to 80 weight percent, based on the total weight of the polyepoxide resins. The aromatic polyepoxide resin is present in the adhesive composition in an amount of from 80 to 20 weight percent, based on the total weight of the polyepoxide resins. In another embodiment, the adhesive composition further comprises a toughening agent.

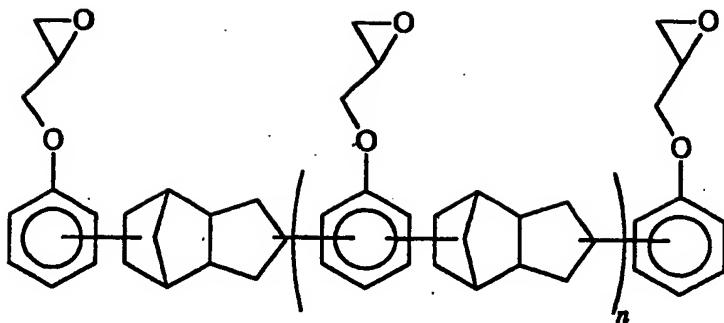
10

Detailed Description of the Preferred Embodiments

The adhesive compositions of the invention contain at least one cycloaliphatic-containing polyepoxide resin. The cycloaliphatic-containing polyepoxide resins have epoxide moieties attached to, that is, pendent from, only aromatic groups and have cycloaliphatic groups between the aromatic groups. A general formula for such compounds is $R(X_n)-R^1-(R(X_p)-R^1)_r-R(X_n)$, where each R is independently at least a divalent aromatic group, each X is an epoxide-containing moiety, each R^1 is independently at least a divalent cycloaliphatic group, and p and r are ≥ 0 and n is at least 1. Examples of such cycloaliphatic groups include the divalent radicals of dicyclopentadiene, cyclopentadiene, norbornane, decalin, and hydrogenated analogs of naphthalene, anthracene, and biphenyl compounds, and combinations thereof. Examples of aromatic groups include mono- and divalent radicals of benzene, naphthalene, bisphenol-A, bisphenol-F, and biphenyl-type compounds, and combinations thereof. The aromatic groups may be substituted, for example, with alkyl groups on the aromatic rings.

25

In some embodiments, adhesives and adhesive compositions of the invention contain one or more dicyclopentadiene-containing polyepoxide resins. Such resins are generally prepared from the reaction of dicyclopentadiene phenol resin and epichlorohydrin under basic conditions. The detailed preparation procedure can be found in publicly available literature. Examples of useful dicyclopentadiene-containing polyepoxide resins have the formula:



wherein n is an integer from 0 to 7 and may be any integer or fraction in between 0 and 7. Epoxide equivalent weights range from 150 to 500. Commercially available 5 dicyclopentadiene-based epoxy resins include HP-7200 from Dainippon Ink and Chemicals, Inc., TACTIX™ 71756 and TACTIX™ 556 epoxy resins, available from Vantico, Inc., Brewster, NY.

Cycloaliphatic-containing polyepoxide resin is present in the compositions of the invention in an amount of from 20 to 80 weight percent of the total weight of the 10 polyepoxide resins present in the adhesive composition, and may be present in any whole or fractional amount between 20 and 80 weight percent. In other embodiments, the cycloaliphatic-containing polyepoxide resin is present in the compositions of the invention in an amount of from 25 to 75 weight percent of the total weight of the polyepoxide resins present, and any whole or fractional amount between 25 and 75 weight percent.

15 Suitable aromatic polyepoxide resins include those containing at least two 1,2-cyclic ethers. Such compounds can be aromatic or heteroaromatic, or can comprise combinations thereof. Suitable polyepoxide resins may be solid or liquid at room temperature. Aromatic polyepoxide resin is used in the adhesives and compositions of the invention to increase the Tg of the cured adhesive film and to provide heat resistance. 20 Aromatic polyepoxide resins do not include polyepoxide resins having both aromatic and cycloaliphatic groups.

25 Compounds containing at least two epoxide groups (that is, polyepoxides) are preferred. A combination of polyepoxide compounds may be employed, and an epoxide resin having a functionality of less than two may be used in a combination so long as the overall epoxide functionality of the mixture is at least two. The polymeric epoxides include linear polymers having terminal epoxide groups (for example, the diglycidyl ether

of bisphenol-A) and polymers having pendent epoxy groups (for example, polyglycidyl ethers of phenolic novolak compounds). It is also within the scope of this invention to use a material with functionality in addition to epoxide functionality but which is essentially unreactive with the epoxide functionality, for example, a material containing both epoxide and acrylic functionality.

A wide variety of commercial epoxide resins are available and listed in "Handbook of Epoxy Resins" by Lee and Neville, McGraw Hill Book Company, New York (1967); and in "Epoxy Resin Technology" by P. F. Bruins, John Wiley & Sons, New York (1968); and in "Epoxy Resins: Chemistry and Technology", 2nd Edition" by C.A. May, Ed., Marcel Dekker, Inc. New York (1988). Aromatic polyepoxides (that is, compounds containing at least one aromatic ring structure, for example, a benzene ring, and at least two epoxide groups) that can be used in the present invention include the polyglycidyl ethers of polyhydric phenols, such as Bisphenol-A or Bisphenol-F type resins and their derivatives, aromatic polyglycidyl amines (for example, polyglycidyl amines of benzenamines, benzene diamines, naphthylenamines, or naphthylene diamines), polyglycidyl ethers of phenol formaldehyde resole or novolak resins; resorcinol diglycidyl ether; polyglycidyl derivatives of fluorene-type resins; and glycidyl esters of aromatic carboxylic acids, for example, phthalic acid diglycidyl ester, isophthalic acid diglycidyl ester, trimellitic acid triglycidyl ester, and pyromellitic acid tetraglycidyl ester, and mixtures thereof.

Preferred aromatic polyepoxides are the polyglycidyl ethers of polyhydric phenols, such as the series of diglycidyl ethers of Bisphenol-A, commercially available from Resolution Performance Products, Houston, TX, for example, under the trade designations "EPON 828" and "EPON 1001F" and the series of diglycidyl ethers of Bisphenol-A and Bisphenol F and their blends, commercially available from Resolution Performance Products, Pernis, The Netherlands, for example, under the trade designations "Epikote 232" and "Epikote 1001". Other useful commercially available aromatic epoxides include the "DER" series of Bisphenol epoxides and "DEN" series of epoxy novolak resins, available from Dow Chemical, Midland, MI; diglycidyl ether of fluorene Bisphenol, available from Resolution Performance Products, Houston, TX, under the trade designation "EPON HPT Resin 1079"; a triglycidyl derivative of p-aminophenol, commercially available from Ciba Performance Polymers, Brewster, NY, under the trade

designation "MY 0500"; a tetraglycidyl derivative of methylene dianiline, commercially available from Ciba Performance Polymers, Brewster, NY, under the trade designation "MY.720"; and a polyfunctional aromatic epoxide resin commercially available from Resolution Performance Products under the trade designation "EPON SU-8." Flame retardant epoxides may also be used, for example, the flame retardant brominated Bisphenol-A diglycidyl ether, commercially available from Dow Chemical, Midland, MI, under the trade designation "DER 580". The term "derivative" as used herein with reference to thermosetting materials refers to a base molecule with additional substituents that do not interfere with the thermosetting curing reaction of the base molecule.

10 Aromatic polyepoxide resin is present in the compositions of the invention in an amount of from 80 to 20 weight percent of the total weight of the polyepoxide resins present in the adhesive composition, and may be present in any whole or fractional amount between 80 and 20 weight percent. In other embodiments, the aromatic polyepoxide resin is present in the compositions of the invention in an amount of from 75 to 25 weight
15 percent of the total weight of the polyepoxide resins present, and any whole or fractional amount between 75 and 25 weight percent.

20 The combination of cycloaliphatic-containing polyepoxide and aromatic polyepoxide resins have a cycloaliphatic character of greater than 10 weight percent. In one embodiment, the cycloaliphatic character is at least 12 weight percent. In another embodiment, the cycloaliphatic character is at least 13.5 weight percent. In another embodiment, the combined polyepoxide resins have a cycloaliphatic character of not more than about 60 weight percent. In another embodiment, the combined polyepoxide resins have a cycloaliphatic character of not more than about 55 weight percent. In another embodiment, the combined polyepoxide resins have a cycloaliphatic character of not more than about 40 weight percent. In other embodiments, the combined polyepoxide resins have a cycloaliphatic character of from greater than 10 weight percent to about 60 weight percent; at least 12 weight percent to about 55 weight percent; and from 13.5 weight percent to 40.5 weight percent, and may be any whole or fractional weight percent in between 12 and 60 weight percent.

30 "Weight percent cycloaliphatic character" is determined by calculating the weight percent cycloaliphatic groups of the cycloaliphatic-containing polyepoxide, excluding the epoxide-containing moieties attached to the aromatic groups. The value, expressed as a

percentage, is then multiplied by the weight percent of cycloaliphatic-containing polyepoxide present in the total amount of polyepoxide resin present in the adhesive composition. For example, if n=1 in the above formula 1, the percent cycloaliphatic character of the cycloaliphatic-containing resin of the formula is 54% (benzene = 5 75.1+76.1+76.1; dicyclopentadiene = 134.2; % cycloaliphatic character = 268.4/(268.4+227.3) = 0.54). If the total amount of cycloaliphatic-containing polyepoxide resins present is 25 weight percent of the total amount of polyepoxide resin, then the polyepoxide resin present in the adhesive composition would have a cycloaliphatic character of 13.5 weight percent (0.54 x 25).

10 The curative for the adhesive films and compositions of the invention is 9,9-bis(3-methyl-4-aminophenyl)fluorene (o-TBAF). o-TBAF is present in the compositions in an effective amount. An "effective amount" of o-TBAF is that amount which cures or crosslinks the polyepoxide resins.

15 The curative is used in the adhesive films and compositions of the invention in a stoichiometric ratio of 0.8 to 1.7 amino hydrogen (NH) equivalents per epoxide equivalent. In one embodiment, a stoichiometric ratio of 1.0 to 1.65 amino hydrogen equivalents per epoxide equivalent is employed. In another embodiment, a stoichiometric ratio of 1.25 to 1.65 amino hydrogen equivalents per epoxide equivalent is used.

20 The adhesives and adhesive compositions of the invention may contain one or more tougheners or toughening agents. The toughening agent can be introduced as a latex of dispersed or synthetic rubber as is disclosed in U.S. Pat. No. 3,316,195 or a graded rubber or core shell rubber particle as disclosed in U.S. Pat. Nos. 3,833,683; 3,856,883; and 3,864,426. The toughening agent can also be introduced into the epoxy resin composition by dissolving reactive elastomers into the epoxy resin which phase-separate during curing. The technique is exemplified by U.S. Pat. Nos. 4,107,116 and 3,894,112. A detailed description of the use of toughening agents in epoxy resin is to be found in the Advances in Chemistry Series 208 titled "Rubbery-Modified Thermoset Resins" edited by C. K. Riew and J. K. Gillham, American Chemical Society, Washington, 1984. One specific toughening agent is the insoluble in situ polymerized elastomeric particles that are formed from amine terminated polyethers, for example, diprimary amine endcapped poly(tetramethyleneoxides). Other examples include amine-terminated butadiene/nitrile rubbers, carboxyl-terminated butadiene/nitrile rubbers, and core shell materials.

The adhesive compositions of the invention may contain from 3 to 20 weight percent of the total weight of the composition of toughening agent. In other embodiments, the adhesive compositions of the invention may contain from 3 to 10 weight percent toughening agent based on the total weight of the composition.

5 Various other adjuvants can also be added the compositions of the invention to alter the characteristics of the cured adhesive. Useful adjuvants include fumed silica, pigments, silica, alumina, magnesium sulfate, calcium sulfate, bentonite, glass beads, glass bubbles, and organic and inorganic fibers. Amounts of up to 80 weight percent of the total weight of the composition adjuvant can be used.

10 The adhesive compositions of the invention are generally useful for bonding substrate where both high peel strength and high shear strength at high temperatures are desired.

Test Methods

Overlap Shear Test

15 The shear strength of the adhesive films of the present invention was determined by bonding two aluminum substrates together using the adhesive film and measuring the shear strength of the resulting construction. More specifically, overlap shear strength was determined according to ASTM D-1002 with the following modifications. The adherends were 2024-T3 bare aluminum panels measuring 7 inches long x 4 inches wide x 0.063 inches thick (178 mm x 102 mm x 1.60 mm).

20 The panels were prepared in the following manner. The panels were first degreased by immersing in alkaline degreaser ("Oakite Aluminum Cleaner 164", Oakite Products Inc., Berkeley Heights, NJ) at about 88 °C for about 10 minutes, followed by rinsing with tap water. The degreased panels were then oxidized by immersing them in a 25 68 °C bath of concentrated sulfuric acid, sodium dichromate and water for about 10 minutes (this is known as Forest Products Laboratories Etch System or FPL Etch System) then rinsing with tap water. This was designated as "Surface Prep 1".

25 In some cases, the panels were further treated as follows. The etched panels were anodized by immersion in phosphoric acid at 22 °C with an applied voltage of 15 Volts for 30 20-25 minutes, followed by rinsing with tap water (test for water break), air drying for 10 minutes at room temperature, then oven drying in a forced air oven at 66 °C for 10

minutes. The resulting anodized aluminum panels were immediately primed within 24 hours of treatment. The anodized panels were primed with a corrosion inhibiting primer for aluminum (3M™ Scotch-Weld™ Structural Adhesive Primer EC-3983, obtained from Minnesota Mining and Manufacturing Company, St. Paul, MN) according to the manufacturer's instructions to give a dried primer thickness of between 0.00010 and 0.00020 inches (2.6 to 5.2 micrometers). The complete surface conditioning procedure was designated "Surface Prep 2".

The primed panels were bonded to one another in an overlapping relationship along their lengthwise dimension using a 15.9 mm wide strip of adhesive film. After removing the liner from one side, the scrim-supported film was applied to the first adherend by hand using a small rubber roller in such a manner as to exclude entrapped air and insure intimate contact between the exposed adhesive and the substrate. After removing the second liner, the second adherend was placed in contact with the exposed adhesive surface to give an assembly with an overlap area of 0.5 inches (12.7 mm). The resulting assembly was fastened together using tape and cured in an autoclave in the following manner. After applying a vacuum to reduce the pressure to 28-30 inches (Hg), about 15 pounds per square inch (psi) (103 kPa) pressure was applied and the temperature of the autoclave was heated from room temperature (68 °F to 77 °F (20 °C to 25 °C)) to 350 °F (177 °C) at a rate of 5°F/min. (2.8 °C/min.). The vacuum was released when the pressure reached about 15 psi (69 kPa). The final temperature and pressure were maintained for 60 minutes before cooling to about 25 °C. The bonded panels were sawn across their width into 1 inch (2.54 cm) wide strips and evaluated for overlap shear strength in accordance with ASTM D-1002 using a grip separation rate of 0.05 inches/minute (1.3 millimeters/minute) using a tensile tester. Testing was conducted at two different test temperatures (room temperature and 177 °C). Samples tested at the elevated temperature were equilibrated for between 10 and 15 minutes prior to testing.

Floating Roller Peel Strength Test

Panels of 2024-T3 bare aluminum measuring 8 inches long x 3 inches wide x 0.063 inches thick (20.3 x 7.6 x 0.16 centimeters), and 10 inches long x 3 inches wide x 0.025 inches thick (25.4 x 7.6 x 0.064 centimeters), were prepared for testing as described above in "Overlap Shear Test". The primed panels were bonded together using the same film

adhesive and cure cycle employed for the overlap shear samples, then evaluated for floating roller peel strength in accordance with ASTM D-3167-76 with the following modification. Test strips measuring 0.5 inch (12.7 cm) wide were cut along the lengthwise direction of the bonded aluminum panels. A tensile testing machine operated at a rate of 5 12 inches/minute (30.5 cm/minute) was used to peel the thinner substrate from the thicker one, and the results normalized to a width of 1 inch.

Materials

CAF 9,9-bis(3-chloro-4-aminophenyl)fluorene, having a theoretical
10 amine hydrogen equivalent weight of 103.3 grams/equivalent.

DER 332 a liquid bisphenol-A based epoxy resin having an epoxide
equivalent of from 172 to 176, available from Dow Chemical
Company, Midland, MI.
15

EPONTM SU-8 a solid polymeric aromatic epoxy resin having an average epoxide
group functionality of around 8, available from Resolution
Performance Products, Houston, TX.

20 TACTIX XP-71756 a dicyclopentadienyl-based epoxy resin, available from Vantico,
Incorporated, Brewster, NY.

UVR 6105 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexylcarboxylate,
having an epoxide equivalent of from 130-135 obtained from Union
25 Carbide, Danbury, CT.

DICY dicyandiamide, available as AmicureTM CG-1200 from Air Products
and Chemicals, Incorporated, Allentown, PA.

30 o-TBAF 9,9-bis(3-methyl-4-aminophenyl)fluorene, having a theoretical
amine hydrogen equivalent weight of 94.5 grams/equivalent.

Rubber Toughener diprimary amine endcapped poly(tetramethylene oxide), number average molecular weight of 7500.

Alumina atomized alumina powder, available as MD-201 from Alcan Metal Powders, Union, NJ.

5

EXAMPLES

Preparation of Resin Compositions

TACTIX™ XP-71756 and SU-8 polyepoxide resins were charged into a 1 gallon (3.8 liter) kneader mixer. The polyepoxide resin mixture was heated, using a steam jacket, to 300 °F (149 °C) with mixing. For Comparative Examples 1-4 and Examples 4 and 5, the DER™ 332 polyepoxide resin was then added with stirring. Next, while continuing to mix and heat the polyepoxide resins at 300 °F (149 °C), a rubber toughening agent preheated to 160 °F (71 °C) was slowly added to the polyepoxide mixture over a period of about 15 minutes. The polyepoxide resin/rubber toughening agent blend was mixed at 300 °F (149 °C) for two hours, then cooled to 250 °F (121 °C) using a water jacket. At this point DER™ 332 polyepoxide resin was then added, if it had not already been done so, with continued mixing. After further cooling to between about 140 °F and 160 °F (60 °C and 71 °C), the fluorene amine curing agent was added in a single charge with mixing, followed by addition of dicyandiamide in the same manner. Finally, in those examples where filler was employed, it was added in a similar fashion as the curing agents. Mixing was continued for 10 minutes at a temperature between about 140 °F and 160 °F (60 °C and 71 °C) after all the components were thoroughly combined.

25

Preparation of Uncured, Liner-supported Adhesive Films

The heated composition from the "Preparation of Resin Compositions" procedure above was coated onto a 0.005 inch (0.13 mm) thick paper liner, having a silicone coating on one side and a polyethylene coating on the opposite side using a knife-over-bed coating station having a gap setting of 0.007 inches (0.18 millimeters) greater than the release liner thickness and a bed and knife temperature of 160 °F (71 °C). The adhesive composition was coated onto the silicone-treated side of the liner to give a liner supported adhesive

film. The adhesive-coated liner was wound up on itself, allowed to stand for 24 hours at room temperature (about 70 °F (21 °C)), then stored at -20 °F (-29 °C) until further use.

Preparation of Uncured, Glass Scrim-supported Adhesive Films

5 Samples of liner-supported film adhesive were equilibrated at room temperature prior to use. One piece of the liner-supported adhesive film, measuring about 11.5 inches (29.2 centimeters) wide and about 36 inches (91.4 centimeters) long, was placed on each side of a glass scrim. The glass scrim employed was either: 1) CS 207, a 1299 style glass fabric having an aminosilane treatment, available from Clark-Schwebel Fiberglass Corp.,
10 White Plains, NY; or 2) 108 E glass fabric finished with S-920 finish, an epoxy silane treatment, available from J.P. Stevens and Co. Inc., Slater, SC, as indicated in Tables 1 and 3 below. This lay-up was passed between two rubber-coated, heated nip rollers at a pressure of about 40 pounds and a temperature between about 140 °F and 160 °F (60 °C and 71 °C) to give a glass scrim-supported adhesive film, also described as an adhesive
15 film having a glass scrim embedded therein, having release liner on each side.

Examples 1-7 and Comparative Examples (CE) 1-9 in Tables 1 and 2 below demonstrate the range of amount of cycloaliphatic epoxy resin that can be used in the compositions of the present invention. The amounts are given in parts by weight (pbw),
20 wherein the combined amounts of all components is 100 pbw. The weight percent aliphatic character was calculated as described above.

Comparative Examples 7-9 were prepared as described above except CAF was used as the curative in place of o-TBAF and UVR 6105 was used in place of TACTIX 71756 in Comparative Example 7. Additionally, Comparative Examples 7 and 8 were also
25 prepared and evaluated using a post cure of 2 hours at 350 °F (177 °C).

TABLE 1

Ex.	DER 332 (wt. %) (% of Epoxy)	TACTIX XP- 71756* (wt. %) (% of Epoxy)	SU-8 (wt. %) (% of Epoxy)	o-TBAF (wt. %) (NH eqvts.)	CAF (wt. %) (NH eqvts.)	DICY (wt. %)	Rubber Toughener (wt. %)	ScrimType	Surface Prep
CE 1	49.6 (100)	0.0	0.0	40.4 (1.50)		1.0	9.0	2	2
CE 2	47.6 (100)	0.0	0.0	42.7 (1.65)		1.0	8.7	2	2
CE 3	25.7 (50)	0.0	25.7 (50)	38.0 (1.50)		1.0	9.6	2	1
CE 4	24.7 (50)	0.0	24.7 (50)	40.3 (1.65)		1.0	9.3	2	1
CE 5	21.6 (41.2)	9.1 (17.5)	21.6 (41.2)	936.9 (1.5)		1.0	9.8	2	2
CE 6	21.1 (41.2)	8.8 (17.5)	13.0 (41.2)	38.5 (1.65)		1.0	9.5	2	2
CE 7	11.9 (25.0)	23.9* (50)	12.0 (25.0)		42.2 (1.50)	1.0	9.0	2	2
CE 8	17.0 (33.3)	25.5 (50)	8.5 (16.7)		38.4 (1.50)	1.0	9.6	2	2
CE 9	16.4 (33.3)	24.6 (50)	8.2 (16.7)		40.6 (1.65)	1.0	9.2	2	2
1a	26.0 (50)	13.0 (25)	12.5 (25)	37.2 (1.65)		1.0	9.8	2	1

Ex.	DER 332 (wt.%) (% of Epoxy)	TACTIX XP- 71756*	SU-8 (wt.%) (% of Epoxy)	α -TBAF (wt.%) (NH eqvts.)	CAP (wt.%) (NH eqvts.)	DICY (wt.%)	Rubber Toughener (wt.%)	ScrimType	Surface Prep
1b	25.1 (50)	12.5 (25)	12.5 (25)	39.4 (1.65)		1.0	9.5	2	2
2	13.5 (25)	27.0 (50)	13.5 (25)	35.0 (1.50)		1.0	10	2	1
3	13.0 (25)	26.0 (50)	13.0 (25)	37.2 (1.65)		1.0	9.8	2	1
4	26.4 (50)	26.4 (50)	0.0 (1.50)	36.2 (1.50)		1.0	9.9	1	1
5	25.5 (50)	25.5 (50)	0.0 (1.65)	38.5 (1.65)		1.0	9.6	1	1
6	6.9 (12.5)	41.5 (75)	6.9 (12.5)	33.3 (1.5)		1.0	10.4	2	2
7	6.7 (12.5)	40.2 (75)	6.7 (12.5)	35.4 (1.65)		1.0	10.0	2	2

* Comparative Example 7 employed the cycloaliphatic resin UVR 6105 in place of TACTIX XP-71756.

TABLE 2

Ex.	Overlap Shear Strength @ R.T. (psi)	Overlap Shear Strength @ 350 °F (177 °C) (psi)	Floating Roller Peel Strength @ R.T. (piw)	% Cycloaliphatic Character in Polyepoxide Mixture
CE 1	3740	1617	19.0	0
CE 2	2907	1057	12.0	0
CE 3	2093	647	23.0	0
CE 4	2133	737	19.0	0
CE 5	3220	2013	7.0	9.5
CE 6	3407	2100	9.5	9.5
CE 7	1769	263	5.5	43.6
CE 8	4727	773	42.0	27.0
	5727*	1740*	42.5*	
CE 9	4040	660	42.0	27.0
	5070*	1553*	39.5*	
1a	3287	1873	26.0	13.5
1b	3400	2700	28.0**	13.5
2	3620	2227	32.5	27.0
3	3333	2593	32.5	27.0
4	4283	2192	32.5	27.0
5	4157	1967	32.5	27.0
6	5050	2860	26.5	40.5
7	4580	2667	25.0	40.5

* after post cure of 2 hours at 350 °F (177 °C).

** data obtained on a second, separate preparation

5 The results in Table 2 demonstrate that compositions of the invention, that is, those whose epoxide component contains above 10% cycloaliphatic character (as defined herein) and whose curing agent is o-TBAF, exhibit a combination of overlap shear values at 350 °F (177 °C) (of at least about 1900 pounds/inch² (psi) (13.1 megaPascals) and Floating Roller Peel Strength peel values (at room temperature) of at least about 20 pounds/inch width (piw) (3.5 Newtons/millimeter). In contrast, compositions containing essentially only difunctional aromatic epoxide resin (for example, DER 332) or a combination of multifunctional and essentially difunctional aromatic epoxide resins (for

10

example, DER 332 and SU-8) do not exhibit such characteristics. Further, compositions employing a cycloaliphatic epoxide component falling outside the definition of cycloaliphatic-containing polyepoxide resin used herein does not exhibit such performance characteristics. In addition, the use of an alternative fluorene/amine curing agent (CAF) in the adhesive compositions does not exhibit such performance characteristics.

The Examples in Tables 3 and 4 below demonstrate that a range of amounts of the epoxy curing agent, o-TBAF, can be employed in the compositions of the invention. A 1299 style glass fabric scrim and 3M™ Scotch-Weld™ Structural Adhesive Primer EC-3983 were employed for these samples.

10

TABLE 3

Ex.	DER 332 (wt.%) (% of Epoxy)	TACTIX XP-71756 (wt.%) (% of Epoxy)	SU-8 (wt.%) (% of Epoxy)	o-TBAF (wt.%) (NH eqvts.)	DICY (wt.%)	Rubber Toughener (wt.%)	Filler (wt.%)
8	17.5 (33)	26.2 (50)	8.7 (17)	27.7 (1.20)	1.0	9.9	9.0
9	16.9 (33)	25.3 (50)	8.5 (17)	30.1 (1.35)	0.9	9.6	8.7
10	16.2 (33)	24.3 (50)	8.1 (17)	32.2 (1.50)	0.9	9.2	9.1
11	15.8 (33)	23.5 (50)	7.8 (17)	34.1 (1.65)	0.9	9.0	8.9

TABLE 4

Ex.	Overlap Shear Strength @ R.T. (psi)	Overlap Shear Strength @ 350° F (177 °C) (psi)	Floating Roller Peel Strength @ R.T. (piw)	% Cycloaliphatic Character in Polyepoxide Mixture
8	4307	2903	30.0	27.0
9	4457	2967	37.5	27.0
10	4450	2860	34.5	27.0
11	4610	2928	38.5	27.0

15

The results in Table 4 show that a range of amounts of epoxy curing agent can be employed in the compositions of the invention. In the examples above, an amount in

excess of stoichiometric was employed. This excess ranged from 1.20 to 1.65 amino hydrogen equivalents per epoxide equivalent. In addition, these examples demonstrate the use of filler to improve shear performance at elevated temperature.

The various modifications and alterations of this invention will be apparent to
5 those skilled in the art without departing from the scope and spirit of this invention. This
invention should not be restricted to that set forth herein for illustrative purposes.

What is Claimed is:

1. A curable adhesive composition comprising a mixture of:
 - a) a mixture of polyepoxide resins comprising at least 20 to 80 weight percent cycloaliphatic-containing polyepoxide resin and from 80 to 20 weight percent aromatic polyepoxide resin, wherein the polyepoxide mixture has a cycloaliphatic character of greater than 10 weight percent; and
 - b) an effective amount of 9,9-bis(3-methyl-4-aminophenyl)fluorene.
- 10 2. The adhesive composition according to claim 1 further comprising a toughening agent.
- 15 3. The adhesive composition according to claim 1 wherein the aromatic epoxy resin is selected from the group consisting of polyglycidyl ethers of polyhydric phenols; aromatic polyglycidyl amines; polyglycidyl ethers of phenol formaldehyde resole resins; polyglycidyl ethers of phenol formaldehyde novolak resins; resorcinol diglycidyl ether; polyglycidyl derivatives of fluorene-containing resins; glycidyl esters of aromatic carboxylic acids; and mixtures thereof.
- 20 4. The adhesive composition according to claim 1 wherein the 9,9-bis(3-methyl-4-aminophenyl)fluorene is present in the adhesive composition in an amount from 0.8 to 1.7 amino hydrogen (NH) equivalents per epoxide equivalent.
- 25 5. The adhesive composition according to claim 1 wherein the cycloaliphatic-containing polyepoxide resin has the formula:
$$R(X_n)-R^1-(R(X_p)-R^1)_r-R(X_n)$$
where each R is independently at least a divalent aromatic group, each X is an epoxide-containing moiety, each R¹ is independently at least a divalent cycloaliphatic group, and p and r are ≥ 0 and n is at least 1.

30

6. The adhesive composition according to claim 1 wherein the aromatic polyepoxide resin is selected from the group consisting of diglycidyl ethers of Bisphenol-A; diglycidyl

ethers of Bisphenol-F; epoxy novolak resins; diglycidyl ether of fluorene Bisphenol; triglycidyl derivatives of p-aminophenol; and combinations thereof.

7. The adhesive composition according to claim 2 wherein the toughening agent is
5 selected from the group consisting of amine terminated polyethers, amine-terminated butadiene/nitrile rubbers, carboxyl-terminated butadiene/nitrile rubbers, core shell materials, and combinations thereof.

8. The adhesive composition according to claim 2 wherein the toughening agent is
10 present in an amount of from 3 to 20 weight percent of the total weight of the adhesive composition.

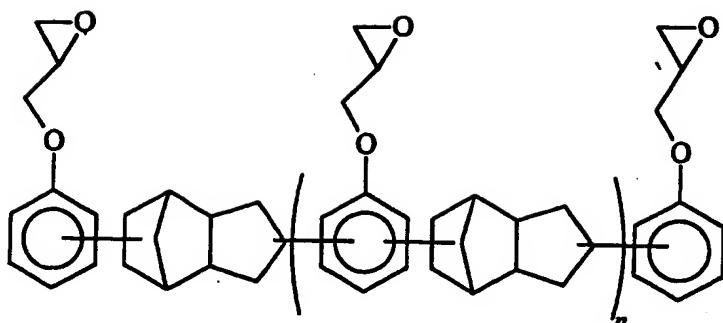
9. The adhesive composition according to claim 1 wherein the cycloaliphatic-containing polyepoxide resin is present in an amount of from 25 to 75 weight percent
15 based on the total weight of polyepoxide resin.

10. The adhesive composition according to claim 1 wherein the aromatic polyepoxide resin is present in an amount of from 75 to 25 weight percent based on the total weight of polyepoxide resin.
20

11. The adhesive composition of claim 1 wherein the weight percent cycloaliphatic character of the polyepoxide resins is not more than 60 weight percent.

12. The adhesive composition of claim 1 wherein the weight percent cycloaliphatic character of the polyepoxide resins is from greater than 10 to about 60 weight percent.
25

13. The adhesive composition of claim 1 wherein the cycloaliphatic-containing polyepoxide resin has the formula:



wherein n is an integer from 0 to 7.

5 14. The adhesive composition according to claim 13 wherein the aromatic polyepoxide resin comprises diglycidyl ether of Bisphenol A.

10 15. The adhesive composition of claim 1 wherein the polyepoxide resins have an aliphatic character of from 12 to 55 weight percent.

15 16. The adhesive composition of claim 14 wherein the polyepoxide resins have a weight percent cycloaliphatic character of 13.5 to 40.5.

20 17. The adhesive composition of claim 2 wherein the toughening agent comprises amine terminated polyether.

25 18. The adhesive composition of claim 17 wherein the cycloaliphatic-containing polyepoxide resin has the formula:

$$R(X_n)-R^1-(R(X_p)-R^1)_r-R(X_n)$$

where each R is independently at least a divalent aromatic group, each X is an epoxide-containing moiety, each R¹ is independently at least a divalent cycloaliphatic group, and p and r are ≥ 0 and n is at least 1.

19. The adhesive composition of claim 18 wherein the aromatic polyepoxide resin is selected from the group consisting of polyglycidyl ethers of polyhydric phenols; aromatic polyglycidyl amines; polyglycidyl ethers of phenol formaldehyde resole resins;

polyglycidyl ethers of phenol formaldehyde novolak resins; resorcinol diglycidyl ether; polyglycidyl derivatives of fluorene-containing resins; glycidyl esters of aromatic carboxylic acids, and mixtures thereof.

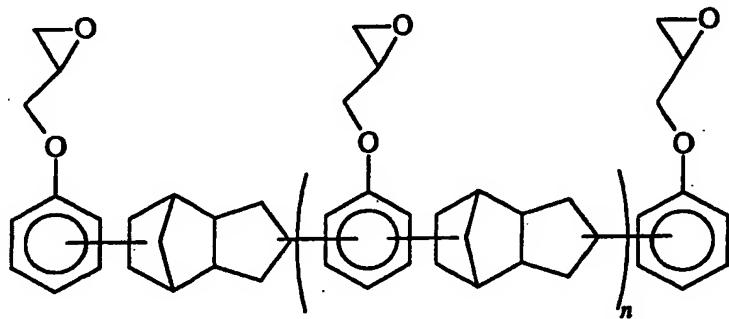
5 20. The adhesive composition of claim 17 wherein the cycloaliphatic character of the polyepoxide mixture is not more than 60 weight percent.

10 21. The adhesive composition of claim 17 wherein cycloaliphatic character of the polyepoxide mixture is at least 12 weight percent and not more than 55 weight percent.

15 22. The adhesive composition of claim 17 wherein the cycloaliphatic character of the poxyepoxide mixture is from 13.5 to 40.5 weight percent.

23. The adhesive composition of claim 22 wherein the cycloaliphatic-containing

15 polyepoxide has the formula:



wherein n is an integer from 0 to 7.

20 24. The adhesive composition of claim 23 wherein the aromatic polyepoxide resin comprises diglycidyl ether of Bisphenol-A.

INTERNATIONAL SEARCH REPORT

International Application No-

PCT/US 02/30155

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 C09J163/00 C08K5/18 C09J7/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHEDMinimum documentation searched (classification system followed by classification symbols)
 IPC 7 C09J C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 00 39189 A (3M INNOVATIVE PROPERTIES CO) 6 July 2000 (2000-07-06) page 29, line 7 - line 10; claims 1-3,5 —	1,3,4,6, 14
A	EP 0 203 828 A (MINNESOTA MINING & MFG) 3 December 1986 (1986-12-03) cited in the application page 3, column 4, paragraph 1; claims 1-3,10; examples —	1,6
A	US 5 639 808 A (COGGIO WILLIAM D ET AL) 17 June 1997 (1997-06-17) example 7 — —/—	1,4,6

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the International filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the International filing date but later than the priority date claimed

- *T* later document published after the International filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- *a* document member of the same patent family

Date of the actual completion of the International search

13 November 2002

Date of mailing of the International search report

20/11/2002

Name and mailing address of the ISA
 European Patent Office, P.B. 5818 Patentlaan 2
 NL - 2280 HV Rijswijk
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
 Fax. (+31-70) 340-3016

Authorized officer

Engel, S

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 02/30155

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 96 33248 A (MINNESOTA MINING & MFG ;KAWATE KOHICHIRO (JP); ISHII SHIGEYOSHI (J) 24 October 1996 (1996-10-24) page 3, line 22 -page 4, line 2; claims 1,5,9; example 1 _____	1,3,4,6

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 02/30155

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
WO 0039189	A 06-07-2000	US	6294270 B1	25-09-2001
		AU	6254199 A	31-07-2000
		CN	1337975 T	27-02-2002
		EP	1141073 A1	10-10-2001
		WO	0039189 A1	06-07-2000
		US	2002001720 A1	03-01-2002
		US	2002114969 A1	22-08-2002
EP 0203828	A 03-12-1986	CA	1264476 A1	16-01-1990
		DE	3669878 D1	03-05-1990
		EP	0203828 A1	03-12-1986
		JP	1911775 C	09-03-1995
		JP	6039520 B	25-05-1994
		JP	61283617 A	13-12-1986
		US	4684678 A	04-08-1987
US 5639808	A 17-06-1997	DE	69510518 D1	05-08-1999
		DE	69510518 T2	30-03-2000
		EP	0708141 A2	24-04-1996
		JP	8225714 A	03-09-1996
		US	5652285 A	29-07-1997
WO 9633248	A 24-10-1996	JP	8291278 A	05-11-1996
		AU	5383996 A	07-11-1996
		DE	69603177 D1	12-08-1999
		DE	69603177 T2	18-11-1999
		EP	0821717 A1	04-02-1998
		WO	9633248 A1	24-10-1996